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OUTGASSING TESTS IN SUPPORT OF
A PROPOSED ASTM SPECIFICATION

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ABSTRACT

The data gathered from three different laboratories by the technique of determining the weight loss in vacuum at 125°C and of collecting the volatile condensable materials at 25°C in vacuum is presented. Two sets of eight commercial samples were tested as was one commercial material prepared to help resolve some variations in results.

A preliminary outgassing specification has been submitted to Committee E-21 on Space Simulation via E. N. Borson for critique and revisions, and it now has gone through two revisions. A data gathering round robin type of measurement was started with the participation of laboratories at Jet Propulsion Laboratory (JPL), Pasadena, California and at European Space Research and Technology Centre (ESTEC), headquartered in Holland, though the apparatus is located near Madrid, Spain. A group of eight commercial materials were distributed to the three laboratories from Goddard Space Flight Center (GSFC) and a second group of eight materials were distributed from ESTEC. Each laboratory conducted the outgassing tests in similar equipment reproduced from that developed at Stanford Research Institute.

Stanford Research Institute personnel, under Contract No. 950745 from JPL during the period from June 1964 to August 1967, developed the technique of determining the percent total weight loss and the percent volatile condensable materials. The primary objective of that program was "to assist the Jet Propulsion Laboratory in the selection of polymeric materials to be used in the construction of spacecraft" (Reference). The technique consisted of subjecting micro-gram quantities of materials to a simulated spacecraft environment as a means of rapid screening of these materials.

Ref. *Polymers for Spacecraft Applications* by R. F. Muraca & J. S. Whittick, Final Report, JPL Contract 950745, p. 1, 9/15/67.

The Apparatus

The particular apparatus devised consisted of a solid copper bar in which was machined twelve sample chambers. Each sample chamber is 15.8 mm (0.625") diameter, 11 mm (7/16") deep and tapering to a 6 mm (0.250") diameter exit port. The back of the sample chamber is removable for inserting the sample and closure is made with a solid copper cover; the exit port is the opening through which volatiles escape. The copper bar is heated to 125°C by means of resistance heaters brazed to the bar. A minimum of two thermocouples are attached to each heater bar, for controlling and recording temperatures.

Opposite the exit port of the individual sample chamber is a collector plate cooled to 25°C for the condensation of those volatile materials which will condense. The gases exit from the sample chamber, passing through a hole in a separator plate which is compartmented to prevent cross-contamination, and to the cooled collector plate. The distance from the exit port to the front surface of the collector plate is approximately 12 mm (0.475 inches). The collector plate is usually metallic with a plated surface, or it may be a salt-flat for use in obtaining infrared spectra. The condenser plate is maintained at 25°C and, with good thermal contact with the back of the metallic collector plate or with the back of a metallic device holding the salt flat, the collector plates are also at 25°C.

Test Method

Various polymeric materials, such as potting compounds, adhesives, and paints can be tested for outgassing. The sample should be prepared in the same manner as they will be used. The solid potting compounds should be cut into small pieces on the order of 3 to 6 mm (1/8" to 1/4") on a side. Adhesives, usually applied in thickness of 0.07 to 0.12 mm (0.003 to 0.005 in.) with only the edges exposed, should be applied between preweighed pieces of aluminum foil for curing, which can then be cut or folded to fit into the sample boat. Paints may be applied to a polyethylene or Teflon sheet from which the paint could be stripped.

The discardable sample boat is made of aluminum foil pressed into shape and degreased, cleaned, and dried. The sample, of between 200 and 300 milligrams, is placed into a pre-weighed boat and then preconditioned for 24 hours in a 50% relative humidity (RH) chamber. The starting weight of the sample is obtained after the 50% RH conditioning. The collector plate is also cleaned and dried before being weighed. Sample

boats and collector plates and loaded into their respective heating and cooling bars following weighing.

The vacuum system is capable of being evacuated into the 10^{-6} torr range in about 45 minutes. The heaters raise the temperature of the sample bar to $125^{\circ} \pm 2^{\circ}\text{C}$ in a 60-minute period. The collector bar is maintained at $25^{\circ} \pm 2^{\circ}\text{C}$ by utilizing a thermal exchanger; two thermocouples attached to each cooling bar indicate the cooling bar temperature and its variation. The heating at 125°C is continued for 24 hours after which the heater current is turned off and dry nitrogen let in to cool the bar rapidly. Within two hours the heater bar should have cooled to 50°C , at which time the bell-jar is raised. Samples and collector plates are transferred to dessicators immediately and all are weighed beginning within one-half hour.

Calculations are made, utilizing the starting weights of the boat and the sample and the final weight of the sample and boat, to provide the percentage of Total Weight Loss (TWL). In a similar manner the percentage of volatile condensable materials (VCM) can be calculated as a percentage of the sample starting weight from the weight gained by the individual collector plate.

One additional step may be taken, that of identifying the major compounds in the condensable materials. The use of a salt-flat as a collector permits direct transfer of the salt-flat to the spectrophotometer. Alternately, by washing or dissolving the condensables from the metal collector plate into a clean beaker the solution can then be applied to a separate salt-flat for spectroscopy.

Round Robin I

The eight materials sent from GSFC included a Mylar film often used at JPL as a standard. The other materials consisted of potting compounds 3 mm ($1/8''$) thick and also one paint as a film. The potting compounds were mixed and cured at GSFC by a technician experienced in working with such polymeric materials. One-third of each material was sent to the other two laboratories with the hope that all tests could be begun in the same week. The shipments to California and to Europe were by air freight, and it was presumed that there was little effect on the samples due to changing temperatures and atmospheric pressures.

The results of the first tests are presented in Table I. These do not show the expected uniformity of results but they do show some peculiarities.

TABLE I
RESULTS OF ROUND ROBIN, IA

MATERIAL	TWL Average			VCM Average		
	GSFC	ESTEC	JPL	GSFC	ESTEC	JPL
I. Chemglaze Z-306	0.953	0.91	-	0.007	0.009	-
II. D. C. 93-500	0.068	0.054	0.15	0.000	0*	0
III. Epon 828/Versamid 125	0.370	1.18	2.07	0.004	0.010	0
IV. Epon 828/Versamid 125 post cured	0.426	1.31	2.11	0.001	0.009	0
V. Epon 828/Versamid 125 with glass bubbles	0.375	1.06	2.05	0.001	0.007	0
VI. GE RTV-11	1.701	1.75	1.60	0.371	0.116	0.36
VII. Mylar A Film	0.191	-	0.47	0.002	-	0
IX. Solithane 113/ C113-300	0.222	0.26	0.40	0.004	0.009	0

*0 in the VCM column indicates a weight loss by the collector plate

The Epon 828/Versamid 125 samples gave confusing results. These three sets of samples, one with a room temperature cure, the second with a heat cure, and the third having glass bubbles mixed in, were prepared by the same person, one experienced in mixing polymeric compounds. He prepared thin samples of 125 mm (5-inch) diameter and cut large sections to be sent to our three test laboratories. Assuming that there was random selection of the large pieces sent to each laboratory, the results show a wide, but consistent disparity:

Total Weight Loss, Epon 828/Versamid 125

	GSFC	JPL	ESTEC
No Heat	0.38%	2.07%	1.22%
	0.36	2.06	1.44
	0.38	-	1.18
Heated	0.41	2.10	1.31
	0.43	2.11	1.39
	0.44	-	1.23
With Bubbles	0.36	2.03	1.07
	0.37	2.06	1.08
	0.40	-	1.02

Note that all GSFC samples are low, JPL's are high and ESTEC's are in the middle.

The group of samples received from ESTEC included potting compounds, films, paints on aluminum foil, and mixtures. The results are presented in Table II. The data for the paints on aluminum foil were calculated on the basis of 0.0044 gm/cm^2 of foil; this assumes that the density of the foil and the dimensions of the foil with the paint were known accurately. However, it is recognized that this type of sample is less desirable than a solid piece of material, as the results show.

TABLE II
RESULTS OF ROUND ROBIN, IB

MATERIAL	TWL (Average)			VCM (Average)		
	GSFC	ESTEC	JPL	GSFC	ESTEC	JPL
I. BLS 203	0.741	1.10	1.09	0*	0	0
II. Glassofix 802	4.290	6.78	5.27	0	0	0
III. Kynel 5505	1.487	2.51	2.94	0	0	0
IV. Mylar A Film	0.255	-	0.40	0	-	0
V. Rilsan	0.948	0.99	0.87	0.013	0.018	0
VI. Sellotape 8002	0.895	1.03	1.62	0.223	0.099	0.29
VII. Silcoset 101	1.588	1.57	1.26	0.250	0.071	0.18
VIII. Technoflon	0.433	0.45	0.45	0	0	0

*0 in the VCM column indicates a weight loss by the collector plate.

With the variations in results from these first two groups of samples, a third run was made utilizing the remaining sample materials, including those from both GSFC and ESTEC. These results are in Table III.

It is recognized that the differences within the samples and differences between the laboratories could not be controlled. However, the samples must be considered as samples which might be sent from a contractor who desires data on the suitability of the material for spacecraft use. For this reason, the use of screening criteria are most helpful in selecting materials known to be low in outgassing. The differences in testing techniques between the three laboratories are also of interest.

TABLE III
RESULTS OF ROUND ROBIN, II

MATERIAL	TWL Average		VCM Average	
	GSFC	JPL	GSFC	JPL
I. BSL 203	0.736	0.96	0.026	0.01
II. Epon 828/Versamid 125	0.673	1.52	0.040	0.03
III. Epon 828/Versamid 125 Post cured	0.672	1.32	0.053	0.04
IV. Epon 828/Versamid 125 with glass bubbles	0.564	1.31	0.049	0.02
V. GE RTV-11	1.745	1.58	0.422	0.28
VI. Kynel 5505	1.199	1.49	0.016	0.02
VII. Rilsan	0.741	0.62	0.059	0.03
VIII. Silcoset 101	1.543	0.98	0.231	0.27

A review of information gathered from these three laboratories brought out certain differences between the techniques utilized at the laboratories. These differences included the material of the collector plate, the use of 50% RH or of 65% RH in conditioning the samples, and the existence of a negative weight gain by the collector plate in some instances. These differences may be summarized as follows:

Known Variations

- (a) The surface of the collector plate is different at the three locations, GSFC uses a chromium-plated collector. ESTEC uses a solid salt-flat collector, and JPL uses a solid copper collector.
- (b) GSFC and JPL condition the samples in 50% RH but ESTEC uses a 65% RH atmosphere, each for a 24-hour period.
- (c) At ESTEC, the temperature of the sample was found to be 115°C. They planned to increase the temperature to the 125°C level.
- (e) At GSFC, the observations that condensation occurs on the separator plate and that the collector plate may show a loss or gain in "blank" runs indicate that further refinements in the system are necessary.

In addition, certain questions were raised with regard to the length of time of RH conditioning, the variability within samples,

and the effect of sample size, whether as many small pieces or one large piece.

The question of length of RH conditioning was raised because of the scheduling of the GSFC's weekly tests and the recent change to having some U.S. national holidays on a Monday. In this connection, GSFC carried out tests using longer than 24 hours in the RH chamber. Duplicate samples were used, one being in the RH chamber 96 hours from Friday until Tuesday, the other being in the chamber for the 24 hours from Monday to Tuesday. Twenty-three samples of the 92-hour RH were higher in weight loss and seventeen of the 24-hour RH were higher, the samples showing the large weight loss differences due to the different times of preconditioning were very high in TWL. For example, a sample of 3M 1157 tape with a polyester adhesive had a TWL of 6.08% with a 24-hour preconditioning and a TWL of 6.45% with a 96-hour preconditioning, or a difference of 0.37%. Seven samples showed no TWL difference, ten of fifteen with the 24-hour preconditioning, and twelve of nineteen with the 96-hour conditioning showed TWL differences of 0.10% or less. It appears that the time of 50% RH preconditioning has no significant effect on TWL.

The effect of sample dimensions was also investigated, utilizing the Epon 828/Versamid 125 samples mentioned above. In the rerun of these samples, the GSFC samples in the second run were cut into many small pieces about 1.5 mm on a side (about 1/16" x 1/16" x 1/16") as opposed to the samples in the first tests which were a single piece weighing about 200 milligrams.

TWL, Epon 828/Versamid 125
Particle Size

	GSFC (small pieces)	GSFC (one piece)
No Heat	0.69	0.38
	0.66	0.36
	0.67	0.38
Heated	0.67	0.41
	0.69	0.43
	0.67	0.44
Bubbles	0.55	0.36
	0.55	0.37
	0.59	0.40

Note that the data are higher for small pieces. As a first assumption, it appears that size has a significant effect.

To check this further, a fresh sample of Epon 828/Versamid 125, 50/50 parts by weight, room temperature cured was prepared and tested. The results are as follows:

Sample Dimensions, Epon 828/Versamid 125

Total Sample > 300 milligrams

14 pieces 1.5mm x 1.5mm x 2.2mm (1/16" x 1/16" x 3/32")
TWL = 0.38, 0.37, 0.36

1 piece 6mm x 9mm x 3m (1/4" x 3/8" x 1/8")
TWL - 0.19, 0.18, 0.23

It appears that these results demonstrate, particularly for Epon 828, that the dimension of the sample has an effect upon the weight loss. As expected, the volatile condensable material (VCM) results are also higher, the total VCM being higher for the higher TWL.

In considering the variabilities in the materials themselves, it was realized that separate mixtures of two component polymers had a built-in inconsistency because of the human element in mixing. In order to reduce the variables, it was decided that a one-component sample, DC 3140 which is available from a tube, should be tested, prepared the same day each week for a number of weeks, cured the same length of time, and tested during the next week's run. In addition, the location of the samples in the heater bar was changed, moving the samples to different locations, with a fourth location for the determination of the "blank."

Two results were noted. The VCM data were unuseable because of an unknown amount of condensate upon the separator plate instead of solely on the collector. Though all of the VCM data were greater than 0.34%, the GSFC system must be modified to collect "all" of the condensables.

TABLE IV
DC 3140

Sample	Location	TWL	Avg. of 3	VCM	Avg. of 3
A	1	1.080		0.341	
A	2	1.150	1.126	0.363	0.352
A	3	1.149		0.352	
B	1	0.928		0.347	
B	2	0.928	0.951	0.356	0.369
B	3	0.997		0.404	
C	1	1.003		0.373	
C	2	0.984	1.011	0.357	0.367

TABLE IV(continued)

Sample	Location	TWL	Avg. of 3	VCM	Avg. of 3
C	3	1.047		0.371	
D	5	1.063		0.370	
D	6	1.069	1.076	0.383	0.374
D	7	1.097		0.368	
E	9	1.039		0.356	
E	10	1.051	1.042	0.374	0.369
E	11	1.036		0.376	
F	13	1.169		0.397	
F	14	1.222	1.204	0.463	0.436
F	15	1.221		0.448	
G	17	1.096		0.459	
G	18	1.116	1.119	0.495	0.488
G	19	1.146		0.511	
H	21	1.094		0.431	
H	22	1.109	1.104	0.415	0.420
H	23	1.108		0.414	

Second Round Robin

as a result of the preceding tests, another series of tests was proposed with the three laboratories. This series of tests was intended to provide some answers to the questions previously raised. Specifically, the aim of this second round robin was to evaluate the role of collector plate material and the influence of humidity (RH) conditioning. GSFC uses a chrome-plated collector plate in contrast to the salt flat employed by ESTEC, and JPL uses a Cu plate. Thus, the question of surface energy and attendant sticking coefficient arises relative to VCM deposition. In addition, GSFC and JPL condition samples at 50% RH while ESTEC performs this treatment at 65% RH. Whether this difference in RH conditioning is really significant in the final analysis has not yet been established.

The sample chosen was a Stycast 1090SI with the 24LV catalyst. It was mixed at GSFC as a thin layer about 1.5mm (1/16") thick; after curing, the slab was cut into small cubes of approximately 1.5mm (1/16") dimensions. The samples were distributed as many such pieces, mixed and randomly selected, and requiring ten or more such pieces for each outgassing sample.

The results from this series of tests are presented in Table V.

TABLE V
Stycast 1090SI/24LV

Laboratory	RH	Specimens	Avg. % TWL	Collector	Avg. % VCM
GSFC	50	7	2.186	Cr	0.084
	50	7	1.988	Cu	0.069
	50	7	2.216	Salt-flat	0.131
	65	7	1.934	Cr	0.079
ESTEC	50	7	2.087	Cr	0.078
	65	7	2.21	Cr	0.067
	65	9	2.189	Salt-flat	0.120
JPL	50	7	2.83	Salt-flat	-
	50	7	2.77	Cu	0.156

The lack of data for the JPL salt-flat data is due to the fact that the fragility of the salt-flat resulted in five of the seven collectors being chipped in handling, resulting in weight differences.

The above results were treated statistically, along with the samples of the one-component RTV 3140. Treating each laboratory's data separately, the results are in Table VI. In these calculations the mean, $\hat{\mu}$, and the standard deviation $\hat{\sigma}$, were calculated, using the formulation

$$\hat{\sigma}^2 = \sum_{L=1}^n \frac{(X_i - \bar{\mu})^2}{n - 1}$$

The percent 2σ was also calculated to present an indication of the comparative consistency of the results from each laboratory.

The information from ESTEC on the use of the salt-flat collector should be clarified. By adhering a thermocouple to the front of the NaCl collector, which is about 5mm thick, the temperature of the cooling bar and of the collector could be determined. The cooling bar had to be cooled to about 10°C in order to get the front of the NaCl collector to 25°C . Also, when the cooling bar was held at 25°C , the front of the collector was at about 31°C . The data above from ESTEC show that the average VCM with the NaCl collector at 25°C was 0.120%, and was 0.033% when the NaCl collector was at 31°C .

TABLE VI

GSFC Sample	n	TWL $\hat{\mu}$	$\hat{\sigma}$	%2 σ	Collector	$\hat{\mu}$	VCM $\hat{\sigma}$	%2 σ
RTV 3140	24	1.079	0.0779	15.6	Cr	0.397	0.048	24.0
Stycast-65%	7	1.934	0.049	5.0	Cr	0.079	0.015	38.0
Stycast-50%	7	1.988	0.074	7.4	Cu	0.069	0.008	23.0
Stycast-50%	7	2.190	0.059	5.4	Cr	0.084	0.021	48.0
Stycast-50%	7	2.216	0.059	5.2	NaCl	0.131	0.024	37.0
ESTEC								
Stycast-65%	9	2.189	0.087	7.95	NaCl	0.120	0.068	113.0
Stycast-65%	7	2.210	0.092	8.3	Cr	0.067	0.020	60.0
Stycast-50%	7	2.087	0.067	6.4	Cr(3)	0.078	0.015	39.0
					NaCl(4)*	0.033	0.018	110.0
JPL								
Stycast-50%	7	2.83	0.054	3.8	-	-	-	-
Stycast-50%	7	2.77	0.029	2.1	Cu	0.156	0.018	23.0

* NaCl flat was known to be above 25°C.

The wide discrepancies in the %2 σ column from each laboratory is unexpected. The lowest value was 23.0% using a copper collector for the Stycast sample while the greatest deviation was in the 100% range using a salt-flat collector. The consistency in the TWL values is much better, with the percent 2 σ ranging from 2.1% to 9.6% for the Stycast samples.

One other possibility as a collecting surface was that of a gold-plated collector which arises from data generated at Lockheed Missiles and Space Company. This laboratory was sent a quantity of the Stycast which was tested by the VCM apparatus and also by a modified thermogravimetric balance. Their results following a 24-hour 50% RH equilibration were as follows:

Method	TWL, %	VCM, %
VCM Device	2.20	0.25
VCM Device	2.19	0.24
VCM Device	2.14	0.24
Thermal Gravimetric Device		
a 12mmx3mm($\frac{1}{2}$ "x1/8")piece	1.39	0.23
Many Small Cubes	2.03	0.26

The most interesting information is the uniformity of the VCM results by different techniques. In order to verify these results, gold-plated collectors were used at GSFC and compared with chromium-plated collectors. The results were as follows:

Sample Position	TWL, %	Collector	VCM, %
#1	2.307	Cr	0.063
#2	2.203	Cr	0.065
#3	2.260	Cr	0.070
#4	2.400	Au	0.091
#5	2.332	Au	0.086
#6	2.226	Au	0.080

These results do not verify the higher VCM obtained at Lockheed, nor do they answer any questions.

As a result of these tests, it is apparent that certain additional testing must be done. The collector material must be standardized, though the handling problems with the salt-flat and the thermal conductivity of the salt-flat indicate the preference for a metallic collector. As a consequence, tests on the use of the gold-plated collector and the use of a roughened versus smooth chromium-plated collector are being done. In addition, means to avoid deposition of material on the separator plate by better collimation of the condensables or by enlarging the hole in the separator plate are being investigated. It is noteworthy that those materials having VCM greater than the desirable maximum of 0.10% will also have visually detectable condensation on the separator plate; the use of the RTV 3140 which had at least 0.397% VCM only points out that the material on the separator plate would make the VCM even greater than 0.397%. In a similar manner, the use of six decimal places in weighing and the calculation to 0.001% is too sensitive when one considers the variability in the one-component RTV 3140 which had a mean of 1.079% in TWL and had 15.6% 2σ variation. One might have expected better consistency in a material which does not require the addition of a catalyst or the mixing together of components. The present results have helped to point out where certain improvements should be made.